Title: Photocarrier transport in undoped microcrystalline silicon studied by the modulated photocurrent technique

Author(s): Hattori, K.; Musa, Y.; Murakami, N.; Deguchi, N.; Okamoto, H.

Citation: Journal of Applied Physics. 94(8) P.5071-P.5082

Issue Date: 2003-10-15

Text Version: publisher

URL: http://hdl.handle.net/11094/2928

DOI: 

Rights:
Photocarrier transport in undoped microcrystalline silicon studied by the modulated photocurrent technique

K. Hattori, a) Y. Musa, N. Murakami, N. Deguchi, and H. Okamoto
Department of Systems Innovation, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

(Received 6 June 2003; accepted 28 July 2003)

A detailed investigation of photocarrier transport and localized states in undoped hydrogenated microcrystalline silicon (μc-Si:H) has been performed using the modulated photocurrent (MPC) technique. The MPC-derived drift mobility shows a systematic variation with crystalline grain size and volume fraction, as well as a distinct anisotropy. The physical implications of these observations are discussed in accordance with models that consider connectivity of crystalline grains and geometry of individual grains. The frequency spectra of MPC mobility and their dependence on excitation intensity are also analyzed in comparison with those observed for hydrogenated amorphous silicon (α-Si:H), leading to a common property of localized states that can explain the experimental results for these materials. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1611638]

I. INTRODUCTION

The transport properties of hydrogenated microcrystalline silicon (μc-Si:H) are a topic of continued interest, from the viewpoints of material physics and technological applications. The material is basically constituted of spherical or columnar Si crystallites with sizes of a few tens of nm embedded in amorphous tissue.1,2 These crystalline grains often form clusters that tend to grow normal to the substrate. At the grain boundaries and at the cluster surfaces, there may exist an increased structural disorder that brings about the occurrence of localized states of various types. Owing to such a complicated situation, the transport properties of μc-Si:H are not determined or predicted straightforwardly. In particular, understanding photocarrier transport, which is crucial for solar cell applications, remains far from being complete.

Although various techniques have been utilized to investigate photocarrier transport in μc-Si:H materials experimentally,3–10 some of these methods have essential limitations. Steady-state photoconductivity and photocarrier diffusion length determined from it are frequently employed to characterize transport properties.3,4,7,10 Normally, they represent the product of carrier mobility and recombination lifetime, the contributions of which are not easily decoupled in the experiments. The time-resolved experiments are capable of measuring these transport parameters separately.5,6,8,9 However, most of the existing tools can apply only in their specific experimental configurations, which tend to restrict the knowledge obtained from the measurements. Specifically, the possible anisotropy in photocarrier transport4,7 has not been addressed so far with a single experimental technique.

We have applied the modulated photocurrent (MPC) technique11–16 to investigate photocarrier transport in undoped μc-Si:H. The photocarrier drift mobility measured with coplanar and sandwich electrode configurations shows a systematic variation with crystalline grain size and volume fraction, as well as a distinct anisotropy. We present simple models that explain the observations reasonably well. The frequency spectra of MPC-derived mobility and their dependence on photoexcitation intensity provide a quantitative assessment of localized states that affect transport. By comparing with the results for hydrogenated amorphous silicon (α-Si:H), we deduce a common property of localized states contained in these materials.

II. EXPERIMENT

A. Sample details

A series of undoped μc-Si:H samples was prepared by a very high frequency glow discharge at 100 MHz with 4.5% dilution of SiH4 in hydrogen.17 The substrate temperature during the deposition was 180 °C. The film crystallinity and microstructure were varied by changing the deposition pressure between 0.08 and 1 Torr. Coplanar Al electrodes with a gap of 1 mm were evaporated on the top of the sample deposited on a glass substrate to investigate photocarrier transport parallel to the substrate. The sandwich structure employed for studying perpendicular transport consists of ZnO/n-type μc-Si:H/undoped, μc-Si:H/n-type μc-Si:H/SnO2/glass. The thickness of the undoped μc-Si:H layer was kept constant at 2 μm for all the samples. An undoped rf-glow discharge α-Si:H sample with coplanar electrodes was also employed in the experiment as a reference.

The structural properties of μc-Si:H samples were characterized by x-ray diffraction and Raman scattering measurements. The x-ray diffraction lines corresponding to (111), (220), and (311) lattice planes were observed for all the samples. The average size of crystallites δhkl was calculated from the angular width of the (hkl) diffraction peak by

---

a)Author to whom correspondence should be addressed; electronic mail: hattori@ee.es.osaka-u.ac.jp
using Scherrer’s formula. In the calculation, the instrumental 
broadening estimated from the measurement of 
pounded monocrystalline Si was taken into account.\textsuperscript{18} The crystallo-
graphic orientation was analyzed in terms of the normalized 
intensity defined as
$$I_{\hkl} = \frac{I_{\hkl}}{\sum I_{\hkl}}$$
subject to the sum rule that
$$\Sigma I_{\hkl} = 1$$
where $I_{\hkl}$ denote the diffraction intensity measured for the sample and 
the theoretical value for random orientation, respectively. 
The summation is taken over the three diffraction lines ob-
erved. Therefore, for instance, $p_{(hkl)}$ larger than 1/3 means preferential growth of $(hkl)$-oriented grain. The Raman spec-
trum was fitted with three Gaussian bands centered around 
520 cm$^{-1}$ (transverse optical phonon in crystalline phase), 
510 cm$^{-1}$ (intermediate region), and 480 cm$^{-1}$ (amorphous phase), 
the integrated intensities of which yielded a semi-
quantitative measure of the crystalline volume fraction $\chi_c$ in 
the usual manner.\textsuperscript{1}

The results of structural characterization for the samples 
deposited directly on glass substrates are summarized graphi-
cally in Fig. 1, where the normalized intensity and the crys-
tallite size are plotted as a function of the crystalline volume 
fraction. As shown in the figure, the volume fraction varies 
between $\chi_c = 36\%$ and $73\%$. Most of the samples (indicated by circles) exhibit (220) preferential orientation, which 
becomes more distinct for a larger volume fraction. For this 
class of samples, the grain size $\delta_{220}$ increases from 17 to 36 
nm monotonously with the volume fraction, while the grain 
size $\delta_{111}$ remains almost unchanged as small as 6 nm. A 
few samples deposited at low pressure (indicated by tri-
angles) have different structural properties. They contain ran-
domly oriented and small size grains ($\delta_{220} \equiv \delta_{111} \equiv 7$ nm) 
with a volume fraction $\chi_c \equiv 50\%$. The results of character-
ization of a set of sandwich samples are similar.

B. Experimental techniques

Here we present a brief explanation of the MPC technique.\textsuperscript{13–16} In the experiment, a semiconductor sample is illuminated homogeneously with a weakly absorbed band-
gap light. The continuity equation is then represented as
$$\frac{dn}{dt} = g(t) - r(t),$$
where $n$ is the total density of photoexcited electrons being 
equal to the total density of photoexcited holes due to charge 
neutralitity, $g$ the photogeneration rate, and $r$ the recombination 
rate. For an excitation light varying in time sinusoidally, 
to first order, all the quantities appearing in Eq. (1) can be 
written in the form $f(t) = f + f(\omega) \exp(i\omega t)$. The modulated 
part of the photocarrier density is simply expressed as
$$\tilde{n}(\omega) = \frac{g(\omega) \tau(\omega)}{1 + i \omega \tau(\omega)}.$$ 
with the average lifetime for all the charge carriers defined as 
$$\tau(\omega) = \tilde{n}(\omega)/\tilde{f}(\omega).$$ 
The conductivity is also separated into 
two components such that $\sigma(\omega) = \tilde{\sigma} + \tilde{\sigma}(\omega) \exp(i\omega t)$. The modulated 
photoconductivity is formally written as
$$\tilde{\sigma}(\omega) = q \mu(\omega) \tilde{n}(\omega),$$
where $q$ denotes the unit electronic charge, and $\mu(\omega)$ is the 
drift mobility that represents the average mobility for all the 
charge carriers. On the basis of the phenomenological con-
sideration described above, we finally define the MPC mobility as
$$\mu_{MPC}(\omega) = \frac{i \omega \tilde{\sigma}(\omega)}{q \tilde{g}(\omega)} = \mu(\omega) \frac{i \omega \tau(\omega)}{1 + i \omega \tau(\omega)},$$
which coincides with the drift mobility $\mu(\omega)$ in the high 
frequency region where the condition that $\omega \tau(\omega) \gg 1$ is 
fulfilled. On the other hand, in the low-frequency region where 
$\omega \tau(\omega) \ll 1$, the MPC mobility is reduced to $i \omega \mu(\omega) \tau(\omega)$. 
In this extreme limit, the modulated photoconductivity $\tilde{\sigma}(\omega)$ is 
in phase with the excitation $\tilde{g}(\omega)$. In other words, the 
carrier system remains in a quasisteady state during modula-
tion and thereby the transport parameters $\mu(\omega)$ and $\tau(\omega)$ be-
come real numbers and frequency independent.

Experimentally, a sinusoidal excitation for the MPC 
measurements was provided by a laser diode with a wave-
length of 678 or 840 nm. The modulation frequency was 
varied between $\omega/2\pi = 10$ Hz and 40 MHz. The amplitude of 
modulated photoconductivity and its phase shift with respect 
to the excitation were detected by a standard lock-in ampli-
ifier for low frequencies ($<100$ kHz) or a rf lock-in amplifier 
for high frequencies ($>10$ kHz). The voltage applied be-
tween the electrodes was chosen in the range where the 
current–voltage characteristic was linear. In this article, the 
MPC mobility data are presented in the form $\text{Re}\{\mu_{MPC}(\omega)\}$, 
which enables us to clearly distinguish the high and low 
frequency regimes. Using the same experimental apparatus,
the frequency dependence of admittance under steady-state illumination was measured concomitantly. All the experiments were performed at room temperature.

III. DRIFT MOBILITY MEASUREMENTS

A. Parallel transport

Figure 2 displays the frequency spectra of MPC mobility measured in the coplanar electrode configuration for the steady-state photogeneration rate \( g = 1 \times 2 \times 10^{20} \, \text{cm}^{-3} \, \text{s}^{-1} \). The upper panel of the figure shows the results obtained with 678 nm excitation for samples with various structural properties. The lower figure compares the results for different excitation wavelengths, 678 and 840 nm. The crystalline grain size \( \delta_{(220)} \) and volume fraction \( \chi_c \) are indicated.

The 678 nm light, which has an energy (1.83 eV) larger than the band gap of the crystalline (1.11 eV) and amorphous (1.75 eV) phases, excites carriers in both of them, whereas photoexcitation from the 840 nm (1.48 eV) light predominantly takes place in the crystalline phase. The experiments showing no discernible difference in the MPC mobility imply that photocarriers generated in the amorphous phase are mainly injected into the crystalline phase via diffusion, and hardly return to the amorphous phase due to finite band edge discontinuities between these phases. Assuming the electron drift mobility in the amorphous phase to be 1 cm²/V s, the root-mean-square distance traveled by a diffusing electron is estimated to 160 nm in a time scale of 10 ns, which corresponds to the maximum modulation frequency of the experiment. For a sufficiently high excitation, the diffusion of charge carriers becomes ambipolar and controlled by holes with a lower mobility. According to the multiple trapping model, the hole drift mobility is calculated to be about 5 \times 10^{-3} \, \text{cm}²/\text{V s} at 10 \, \text{ns}. This amounts to an ambipolar diffusion length of 10 nm. These estimated values of diffusion length are larger than or comparable to a mean spacing between grains for our samples, which is evaluated to be \( \Delta = 6-7 \, \text{nm} \) at most, based on the following relation: \( \chi_c \approx 1/(1 + \Delta/d) \). The comparison of the characteristic lengths reasonably explains that photocarriers are substantially accumulated in crystalline phase.

Carrier transport in any inhomogeneous media is essentially statistical, and could be illustrated in the context of the percolation theory. A simple model for carrier transport in \( \mu_c-\text{Si:H} \) is to consider that connected crystalline grains form a percolation channel through which current flows effectively. The percolation probability that a given grain is effectively connected to the rest to be available for carrier transport on a macroscopic scale increases with the volume fraction above a certain threshold. The percolation-limited transport in \( \mu_c-\text{Si:H} \) may also depend on the dimension of grains. For example, it is likely that large size grains make grain-to-grain carrier transfer more efficient because of their larger contact area. The other important factors to be

FIG. 2. Frequency spectra of MPC mobility measured in the coplanar electrode configuration for the steady-state generation rate \( g = 1 \times 2 \times 10^{20} \, \text{cm}^{-3} \, \text{s}^{-1} \). The top part summarizes the results obtained with 678 nm excitation for samples with various structural properties. The bottom part compares the results for different excitation wavelengths, 678 and 840 nm. The crystalline grain size \( \delta_{(220)} \) and volume fraction \( \chi_c \) are indicated.

The crystalline volume fraction dependence of 10 MHz drift mobility measured in coplanar (\( \parallel \)) and sandwich (\( \perp \)) configurations. The data for samples with large crystalline grains (\( \delta_{(220)} \geq 17 \, \text{nm} \)) are plotted as circles and those with small grains (\( \delta_{(220)} \approx 7 \, \text{nm} \)) as triangles. The results of measurements for the sandwich structure (\( \times \)) are corrected in accordance with the equivalent circuit model (\( \bigcirc \)). The dotted lines are drawn to guide the eye.

FIG. 3. The crystalline volume fraction dependence of 10 MHz drift mobility measured in coplanar (\( \parallel \)) and sandwich (\( \perp \)) configurations. The data for samples with large crystalline grains (\( \delta_{(220)} \geq 17 \, \text{nm} \)) are plotted as circles and those with small grains (\( \delta_{(220)} \approx 7 \, \text{nm} \)) as triangles. The results of measurements for the sandwich structure (\( \times \)) are corrected in accordance with the equivalent circuit model (\( \bigcirc \)). The dotted lines are drawn to guide the eye.
considered are localized states at which traveling carriers can be trapped as well as the potential barrier over which carriers propagate, both existing in the grain boundary region. It is apparent that they act as an obstacle for intergrain carrier passage, and affect more seriously transport through a percolation cluster formed with small grains having a large surface-to-volume ratio. These considerations give a qualitative interpretation for the observation that the drift mobility increases with the volume fraction and decreases for smaller grains.

B. Perpendicular transport

1. Photoadmittance

Prior to discussing the results of drift mobility experiments in the sandwich electrode arrangement, we will explain the admittance measured under steady-state illumination. Typical frequency spectra of conductance and capacitance observed for various generation rates $\dot{g}$ are shown in Fig. 4. A staircase-like structure is clearly found in the spectra. The conductance remains constant and low in the low frequency region, and then increases with frequency to reach an intermediate step. In the high frequency region, the conductance once again increases with frequency. An enhanced but reversed behavior is seen for the capacitance spectra. A similar feature was found in the previous admittance study.3

A simpler explanation for the admittance spectra has been introduced by Kocka et al.3 They consider the equivalent circuit of a sample composed of a series combination of admittances: $Y_D(\Omega) = G_D + i\Omega C_D$, which represents the depletion layer near the contact, and $Y_B(\Omega) = G_B + i\Omega C_B$, which represents the remaining volume of the film, and of the contact resistance of the electrodes: $R_C$. Here, $\Omega$ denotes the angular frequency of the alternating current (ac) voltage. The total admittance of the sample to be observed is then $Y_{nc} = Y/(1 + i\Omega R_C)$, where $Y = Y_D Y_B/(Y_B + Y_D)$. The least-square fits to the data are plotted as solid lines. As shown in the figure, the measurements are reasonably well accounted for by this model. The circuit parameters obtained from this procedure are summarized in Fig. 5 as a function of generation rate. Both capacitance components $C_{B,D}$ are almost independent of generation rate. The bulk layer capacitance $C_B$ coincides with its geometrical value (shown by the dotted line) calculated with a dielectric constant of 12, which is typical for Si material irrespective of its structure. In contrast, the depletion layer capacitance $C_D$ is extremely large,

![Fig. 4. Frequency spectra of conductance and capacitance measured for the sandwich structure at various generation rates in the range $\dot{g} = 1.6 \times 10^{15} - 1.6 \times 10^{20}$ cm$^{-3}$ s$^{-1}$. The crystalline grain size $d_{(220)}$ and volume fraction $\chi_c$ are indicated in the figure. The solid lines are theoretical fits to the data in accordance with the equivalent circuit model.](image)

![Fig. 5. Generation rate dependence of circuit parameters derived from the theoretical fits shown in Fig. 4. The dotted line indicates the geometrical capacitance for a dielectric constant of 12.](image)
The dielectric relaxation in the depletion layer, the characteristic frequency of which is estimated to be 100 kHz, affects the measurement. This shows in the phase-shift bump observed at the relaxation frequency, which disappears in the corrected internal response. At high frequencies, an anomalous phase lag exceeding 90° is also corrected in this manner.

Deriving the MPC mobility from the modulated photoconductance is a straightforward calculation. The results obtained from \( \tilde{G}_B(\omega) \) at \( \omega/2\pi = 10 \text{ MHz} \) and \( g = 1 - 2 \times 10^{20} \text{ cm}^{-3} \text{s}^{-1} \) are summarized in Fig. 3, where the calculations from \( \tilde{I}(\omega)/V \) are also plotted for comparison. The figure illustrates that for all the sandwich samples, the presence of a depletion layer and a resistive contact disturbs the measurement to a significant degree, and the correction is quite substantial for evaluating the MPC mobility that represents the photoconductive region in the sample. To simplify, we shall call it the MPC mobility for sandwich samples in the following. The MPC mobility for sandwich samples containing large grains increases with the crystalline volume fraction, similar to the observation for coplanar structures. This feature is a manifestation of the percolation-controlled transport. A striking difference between sandwich and coplanar structures, in which photocarrier transport is monitored perpendicular and parallel to the substrate, respectively, lies in the magnitude of MPC mobility. The MPC mobility is more than ten times larger for perpendicular transport than parallel transport.

The observation is hardly explained by considering homogeneously distributed spherical crystalline grains. The dominant grains included in our samples are oriented in the [220] direction. It is known that, in such a case, individual grains often have an elongated shape along the growth direction. Moreover, during film growth, the grains may form a natural cluster with a columnar structure normal to the substrate. It is then logical to attribute the anisotropy of transport property to the geometry of constituents.

C. Comparison with previous experiments

Previously, the drift mobility in undoped \( \mu \text{c-Si:H} \) materials has been investigated by applying various experimental techniques. Before concluding this section it may be appropriate to compare our experimental results with the previous ones. Traveling wave measurements in the coplanar configuration provided an evaluation of drift mobility in the range 0.1–0.6 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for samples with \( \chi_c \approx 75\% \), which does not differ much from our result. A typical value of 3 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for sandwich samples was obtained in the study using a method called charge extraction by linearly increasing voltage. The result is compatible with the present evaluation, in terms of order of magnitude. Time-resolved microwave conductivity experiment showed that the drift mobility increased from 2 to 9 cm\(^2\) V\(^{-1}\) s\(^{-1}\) monotonously with the volume fraction in the range \( \chi_c = 60\% \sim 90\% \). The measurement utilizes microwave reflection for monitoring photoconductivity of the film in the absence of external electric field, and largely reflects the motion of carriers in their higher mobility direction. An agreement with our evaluation for perpendicular transport is therefore thought to be reasonable. The large-

FIG. 6. Comparison between the measured external response \( \tilde{I}(\omega)/V \) (\( \circ \)) and the calculated internal response \( \tilde{G}_B(\omega) \) (\( \bullet \)) in amplitude and phase shift with reference to the modulated photoexcitation. The correction is based on circuit parameters shown in Fig. 5.
est disparity is found with the transient grating experiment, the result of which indicates that the ambipolar drift mobility exceeds 100 cm²/V s for parallel transport. It must be borne in mind that this kind of experiment proceeds normally with an extremely intense photoexcitation. It is likely that the resulting high-density nonequilibrium carriers significantly influence electronic properties of the grain (or cluster) boundary region, such as screening of potential barriers or saturation of trap occupancy. These side effects may explain the discrepancy in the measurements.

IV. MODEL CONSIDERATION

This section presents a theoretical approach to the physical implications from the drift mobility measurements assuming that all the dimensions of the transport regions are greater than the mean free path of carriers. Therefore, the models to be developed are in principle classical systems as far as the effects of disorder and geometry on transport are concerned. Inclusions of both grains and clusters make the theoretical treatment very complex. We simplify the analysis by assuming either of these subsystems to be a limiting factor determining transport properties. In the following we arbitrarily consider the case when grains and their boundaries dominate transport. The discussion for cluster-limited transport is essentially similar if the cluster dimensions are much smaller than the size of the system.

A. Effective-medium model

The structural inhomogeneity present in disordered materials usually gives significant effects on carrier transport properties. The problem we are dealing with relates to a two-phase random system in which a volume fraction of χc has a conductivity σc (crystalline phase) and the reminder of χa = 1 − χc a conductivity σa (amorphous phase). In that case, the effective-medium theory 24,25 expresses the static conductivity σ of the material as

\[ σ = σ_0 + \sqrt{σ_a^2 + σ_c^2} \sigma_a/2, \]

with \( σ_0 = Σ_{i=c,a}σ_i(1-1/3)/(4/3) \). It is easily shown that the expression has a simple limiting form when \( σ_a/σ_c \rightarrow 0 \) and \( σ_c/σ_a \rightarrow 0 \):

\[ \sigma = \sigma_c \eta(\chi_c), \]

where the function \( \eta(x) \) is written as \( η(x) = (x-1/3)θ(x-1/3)/2/3 \) with the unit step function \( θ(x) \). This produces a linear increase of σ/σc when \( χ_c \gg 1/3 \). The critical value, 1/3, is very close to the percolation threshold, 0.31–0.32, obtained from the numerical computation for a simple cubic network. 24,27 As mentioned in Sec. III B 1, the effective medium theory can calculate the dielectric function that describes the response of the system to ac electric field. In this article, we do not go into incorporating the ac theory, 26 being consistent with the interpretation of admittance spectra, and we base our discussion on Eq. (5) and its extension.

The theoretical formulation is easily extended to the modulated part superposed on the steady-state photocconductivity, giving

\[ \tilde{σ}(\omega) = Σ_{i=c,a} s_i \tilde{σ}_i(\omega), \]

with the coefficient describing a sensitivity of relevant constituent

\[ s_i = \frac{3}{4} (\tilde{σ}(1-1/3) + \tilde{σ}/3), \]

where \( j = a,c \) for \( i = c,a \). It is noted that an equivalent decomposition, \( \tilde{σ} = Σ_i s_i \tilde{σ}_i \), exists for the steady-state conductivity. The volume fraction dependence of the effective-medium conductivity is illustrated in Fig. 7. Analogous to the general result, one finds that \( \tilde{σ}(ω) = \tilde{σ}_c(ω) \eta(χ_c) \) for a negligibly small conductivity of the amorphous phase. Recall that the MPC experiments indicate a substantial accumulation of photocarriers into the crystalline phase. The approximation mentioned above is therefore practically validated for our µc-Si:H samples. Consequently, the high-frequency MPC mobility is formulated as

\[ μ_{MPC}(ω) = μ_c(ω) \eta(χ_c)/χ_c, \]

where \( μ_c(ω) \) denotes the drift mobility in the crystalline phase. The factor \( χ_c^{-1} \) describes the correction for photocarrier density.

The carrier flow in the crystalline phase is considered to be limited by localized states and potential barriers built up at grain boundaries. In order to make the discussion concrete, we shall assume that electrons are the predominant type of carriers in photoconduction. The theoretical analysis on the basis of the Shockley–Read statistics, which postulates that the localized states exchange carriers via the extended band states, yields a concise expression

\[ μ_c(ω) = \frac{μ_c^0}{1 + \int dE N(E) γ_p(E,ω)}. \]

Here, \( μ_c^0 \) is the mobility of free electrons in the conduction band, and \( N(E) \) the density of localized states at an energy \( E \). The function \( γ_p(E,ω) \) describes the modulation of the occupation function due to electron trapping, the details of which are explained in the Appendix. When the electron diffusion length is larger or comparable to the length dimension of grain δ, the function \( N(E) \) given in Eq. (9) is regarded as the areal density of grain-boundary states multiplied by the surface-to-volume ratio, which generally increases for
smaller grains. Equation (9) accounts for the contribution from potential barriers, with the effective mobility, \( \mu^e_p = \nu_0 P/E_{th} \), following from the thermionic field emission model.\(^{28,29}\) Here, \( \nu_0 = \sqrt{kT/2\pi m} \) is the thermal velocity, and \( E_{th} = kT/q \beta \) the thermal field, expressed with the thermal energy \( kT \) and the effective mass of electron \( m \). The factor \( P \) represents the barrier transmission probability involving two possible channels, classical thermionic emission and quantum mechanical tunneling. In the purely classical case, \( P = \exp(-\phi_b/kT) \) for a barrier height of \( \phi_b \).

Theoretical description presented here demonstrates that the boundary-limited drift mobility \( \mu_c \) correlates with the dimension of grains, and tends to lower for smaller grains.

The parallel drift mobility data show a lower value for smaller grains even at a similar volume fraction, implying that the geometrical constraints are substantial. From a series of drift mobility data obtained for samples with large grains, it has been confirmed that the product \( \chi_c \cdot H_{MPC} \) plotted versus \( \chi_c \) forms a straight line. The onset of the line is found to be \( \chi_c \approx 30\% \) for both parallel and perpendicular mobility data. This behavior is in agreement with that expected from Eq. (8) if \( \mu_c \) is independent of \( \chi_c \). The positive correlation between \( \delta \) and \( \chi_c \) observed for our samples, however, implies that \( \mu_c \) should increase with \( \chi_c \), contrary to the observation. This makes us reconsider the geometrical effects. In accordance with Seto model,\(^{28}\) the potential barrier is produced by the space charge formed near the grain boundary, and the barrier height increases with the grain size when the associated interfacial traps are unsaturated. A structural strain in \( \mu_c \cdot Si:H \) which is thought to be relieved by the inclusion of an amorphous phase, becomes highly concentrated in the grain boundary region with increasing crystalline volume fraction. This may be accompanied by the occurrence of a lot of localized states. These additional mechanisms might operate to compensate the possible variation of \( \mu_c \) with \( \chi_c \).

As evident in Eq. (5), the effective-medium theory considers a homogeneous and isotropic substitutive system, and thereby cannot deal with transport anisotropy. In this sense, the argument given above is still oversimplified. Thus, although the present consideration does not provide a rigorous description of carrier transport in \( \mu_c \cdot Si:H \) it still helps understanding the percolation process involved.

B. Random-walk model

Transport anisotropy itself might be accounted for from a different point of view. The simplest model for \( \mu_c \cdot Si:H \) with a sufficiently high crystalline volume fraction is an array of crystalline grains. A good example for analyzing carrier transport is then a Brownian particle on the three-dimensional lattice, where each lattice site is placed at the center of the grains, and the jump of a particle to a nearest-neighbor site is limited by grain boundary. Because of the asymmetrical shape of grains, we suppose here, a simple tetragonal lattice with spacings \( a=b<c, \) where the \( c \)-axis is parallel to the main axis of the grains. In that case, it follows from elemental statistical considerations that the diffusion front of particles generally forms a spheroid. The relevant diffusion coefficient in the direction labeled by \( l=a, b, c \) is simply expressed as \( D_l = w_l l^2 \), where \( w_l \) is the probability of jump in the \( l \)-direction per unit time. This gives an anisotropy represented by the ratio \( D_x/D_{a,b} = (c/a)^2 \) for an isotropic jump probability. Assuming that the jump probability is proportional to a contact area such that \( w_c \approx ab \), one obtains the estimate that \( D_x/D_{a,b} = c/a \). Since the factor \( c/a \) corresponds to the aspect ratio of the grain, the boundary-limited random-walk model reasonably links grain geometry to transport anisotropy.

Although the random-walk model is instructive for understanding transport anisotropy, it does not incorporate the concept of percolation at the present level. To be more general, one has to consider a percolation lattice, where only a fraction of all sites is occupied by grains, the rest being empty. A test particle can move only from an occupied site of the lattice to a nearest neighbor that is also occupied. In this sense, both effective-medium and random-walk models discussed in this article are complementary to each other but clearly insufficient. We believe that a more generalized and sophisticated theory could be derived from extensions of these two basic models.

V. EVALUATION OF LOCALIZED STATES

A. Similarity to amorphous silicon

So far, we have examined the transport mechanism in \( \mu_c \cdot Si:H \) mainly from the drift mobility magnitude measured under a specific condition that \( \omega L/2\pi = 10 \text{ MHz} \) and \( \bar{g} = 1-2 \times 10^{20} \text{ cm}^{-3} \text{ s}^{-1} \). In this section, we discuss the frequency spectra observed at various generation rates, as well as the physical insight derived from them. Typical spectra measured for \( \mu_c \cdot Si:H \) are displayed in Fig. 8, and are compared with the results obtained for \( a \cdot Si:H \). At first sight, one finds that the spectral feature as well as the generation-rate dependence are qualitatively similar for both materials. Each spectrum shows roughly two branches separated by a knee. The frequency at which the knee appears shifts toward the higher frequency side with increasing generation rate. Since the relevant frequency is determined by the average lifetime as described in Sec. II B, the observation is reasonably interpreted in terms of the recombination via localized states populated with nonequilibrium carriers. The high frequency spectra tend to approach a single line, independently of the generation rate. This feature is more clearly identified on the results for \( a \cdot Si:H \). Conversely, an intermediate part between the low-frequency falloff and the high-frequency convergence varies, depending on the generation rate. The magnitude of MPC mobility in this region increases appreciably with the generation rate, so that the spectra cross one another.

B. Numerical calculation

1. Model

The similarity between \( \mu_c \cdot Si:H \) and \( a \cdot Si:H \) led us to carry out a detailed theoretical investigation of the MPC spectra on the basis of the distribution of localized states suggested for \( a \cdot Si:H \). For this purpose, we have performed a numerical calculation. The calculation incorporates the density of states (DOS) consisting of a distribution of dangling
bond (DB) states superposed on band tail (BT) states. The BT-DOS \((N^{BT})\) decays linearly with a slope of 0.1 eV from the respective band edge and thereafter decreases exponentially toward midgap.\(^{14,15}\) The characteristic temperatures describing the exponential parts were chosen as \(T_e = 220\) K for the conduction BT states and \(T_e = 500\) K for the valence BT states. A single Gaussian band with a standard deviation 0.1 eV centered at 0.85 eV from the valence band edge \(\varepsilon_v\) was assumed for the DB–DOS \((N^{DB})\). The correlation energy of DB states was taken as \(U = 0.3\) eV. In thermal equilibrium, singly occupied (neutral) DB occupation prevails within the energy interval between the Fermi level \(\varepsilon_F\) and \(\varepsilon_F - U\). The DB states above \(\varepsilon_F\) are mainly unoccupied (positively charged) while the states below \(\varepsilon_F - U\) are doubly occupied (negatively charged). Charge neutrality in equilibrium is approximately maintained by an equal integrated density of positively and negatively charged DB states, positioning the Fermi level at \(\varepsilon_F = \varepsilon_v + 1\) eV. The total DB density was adjusted so as to give the neutral DB density of \(3 \times 10^{15}\) cm\(^{-3}\) at \(T = 300\) K, which is a typical value for \(a\)-Si:H. At this temperature, the charged-to-neutral defect density ratio was calculated to be 0.15.

The rate equations for the nonequilibrium occupation functions of DB states, \(f^+\) (positively charged), \(f^0\) (neutral), and \(f^-\) (negatively charged), are expressed with the densities of free electrons \(n^f\) and holes \(p^f\) as

\[
\frac{\partial}{\partial t} f^+(\varepsilon,t) = \left[ p^f(t) C^0_p + e^+_n(\varepsilon) \right] f^0(\varepsilon,t) - \left[ n^f(t) C^+_n + e^-_n(\varepsilon) \right] f^+(\varepsilon,t), \tag{10a}
\]

\[
\frac{\partial}{\partial t} f^0(\varepsilon,t) = \left[ n^f(t) C^+_n + e^+_n(\varepsilon) \right] f^-(\varepsilon,t) - \left[ p^f(t) C^0_p + e^-_p(\varepsilon) \right] f^0(\varepsilon,t). \tag{10b}
\]

The electron occupancy of BT states obeys

\[
\frac{\partial}{\partial t} f^-(\varepsilon,t) = \left[ n^f(t) C^+_n + e^+_n(\varepsilon) \right] f^0(\varepsilon,t) - \left[ p^f(t) C^0_p + e^-_p(\varepsilon) \right] f^-(\varepsilon,t). \tag{11}
\]

In the expressions given above, \(e_{n,p}\) are the thermal emission rates for an electron and a hole from BT states, and \(C_{n,p}\) are the associated capture coefficients. The carrier emission rates \(e^0_{n,p}\) and \(e^{+0}_{n,p}\) and the capture coefficients \(C^{+0}_{n,p}\) and \(C^{0-}_{n,p}\) correspond to the DB states, where the superscripts denote charge states as usual. Combining the rate equations with the continuity equations for free carriers

\[
\frac{d}{dt} n^f(t) = g(t) - \int d\varepsilon N^{BT}(\varepsilon) \left[ n^f(t) C^+_n \right] \left[ 1 - f(\varepsilon,t) \right] - e^+_n(\varepsilon) f^-(\varepsilon,t), \tag{12a}
\]

\[
\frac{d}{dt} p^f(t) = g(t) - \int d\varepsilon N^{BT}(\varepsilon) \left[ p^f(t) C^0_p \right] f^0(\varepsilon,t) - e^-_p(\varepsilon) \left[ 1 - f(\varepsilon,t) \right] - f^0(\varepsilon,t) e^+_n(\varepsilon) f^-(\varepsilon,t), \tag{12b}
\]

the solutions for free carrier densities and occupation functions were obtained for a modulated photoexcitation \(g(t) = \tilde{g} + \tilde{g}(\omega) \exp(i\omega t)\).\(^{11,30}\) The MPC mobility discussed below was calculated assuming that photocurrent is dominated by electrons. The charged DB state may have a higher capture efficiency than a neutral one due to Coulomb attraction. To examine this effect on the MPC mobility, the capture coefficient ratio, \(r_{cap} = C^{+0}_{n,p}/C^{0-}_{n,p} = C^-_{n,p}/C^0_{n,p}\), was varied from 1 to 100, while \(C^0_{n,p}\) was kept fixed at \(10^{-8}\) cm\(^2\) s\(^{-1}\). The capture coefficients \(C_{n,p}\) for BT states were assumed to be identical to \(C^0_{n,p}\).

2. Result

The results of the calculations are summarized in Fig. 9, where the MPC mobility Re\([\mu_{MPC}]\) is displayed topographically as a function of frequency \(\omega L/2\pi\) and generation rate \(\tilde{g}\).

The lines correspond to a sequence of mobility values spaced in equal logarithmic steps. The graph is shaded in such a way that regions with higher values are lighter. Three distinctive regions can be observed in the contour map of MPC mobility. At sufficiently high frequencies, the electron transport is mainly controlled by trapping at the conduction BT states.
Since they are distributed near the conduction band edge and have high thermal-emission rates, a quasithermal equilibrium with the conduction band tends to be established promptly. This results in a drift mobility being weakly dependent on frequency, and a plateau-like topography in the corresponding area. The recombination-limited falloff forms a valley in the area with a low frequency and a high generation rate. A hill sloping gradually toward the lower frequency side is found in the area with a low generation rate, which is mainly due to trapping at deep DB states. A significant difference between the results obtained for $r_{\text{cap}} = 1$ and $r_{\text{cap}} = 100$ is found in a medium range of generation rates. For the higher capture coefficient ratio, the BT plateau extends to a lower frequency region, particularly for generation rates ranging from $10^{13}$ to $10^{19}$ cm$^{-3}$ s$^{-1}$ in 1 order of magnitude steps. Simultaneously, the DB hill grows for generation rates $10^{14} - 10^{18}$ cm$^{-3}$ s$^{-1}$. The observation in the contour map is clearly confirmed in Fig. 10, which displays a collection of frequency spectra for generation rates varying from $10^{13}$ to $10^{19}$ cm$^{-3}$ s$^{-1}$ in 1 order of magnitude steps.

The present experiment is therefore an indication that both $\alpha$-Si:H and $\mu c$-Si:H materials contain such defects commonly.

It is well known that the MPC experiment provides a useful means not only to measure the photocarrier drift mobility but also to evaluate the DOS distributions as well as the capture coefficients. The results of such measurements are discussed in the next subsection, and confirm a similarity between defects in $\alpha$-Si:H and $\mu c$-Si:H, in a more quantitative way.

C. Density of states and capture coefficient

Based on Eqs. (10)–(12), the behavior of modulated photoconductivity related to the coexistence of BT and DB states has been theoretically studied in previous works. The analysis derives a high-frequency approximation such that

$$\text{Im}[\bar{g}(\omega)/\bar{n}(\omega)] = \omega + C_n \int_{E_{\text{in}}}^{E_c} d\epsilon N^{\text{(BT)}}(\epsilon) \text{sech}[(\epsilon - \epsilon_0)/kT]/2$$

$$+ C_n \int_{E_{\text{in}}}^{E_c} d\epsilon N^{\text{(DB)}}(\epsilon) \text{sech}[(\epsilon - \epsilon_0)/kT]/2$$

$$+ C_n \int_{E_{\text{in}}}^{E_c} d\epsilon N^{\text{(DB)}}(\epsilon) \gamma(\epsilon) \text{sech}[(\epsilon - \epsilon_0)/kT]/2.$$  \hspace{1cm} (13)

It is noted that the ratio $\bar{g}(\omega)/\bar{n}(\omega)$ on the left-hand side of the equation is equal to $i\omega \mu_{\text{dr}}/\mu_{\text{MPC}}(\omega)$ for $\bar{\sigma}(\omega)$.
= qμn0 2(ω). The equality may not be valid for the MPC mobility measured for μc-Si:H, but the proportionality between g̃(ω)/̃n(ω) and iαMPC(ω) is reasonably assumed, within the framework of the effective-medium model discussed in Sec. IV A. The frequency-dependent emission energies, εw, εw+, and εw−, and the quasi-Fermi levels for trapped electrons, εin, εin+, and εin−, are defined as

\[ ε_w = ε_c - kT \ln(N_v C_n / ω) , \]
\[ ε_w^+ = ε_c - kT \ln(N_v C_n^+ / 2ω) , \]
\[ ε_w^- = ε_c - kT \ln(2N_v C_n^- / ω) - U , \]

and

\[ ε_{in} = ε_c - kT \ln[N_v C_n / (̃n/̃C_n + ̃p/̃C_p)] , \]
\[ ε_{in}^0 = ε_c - kT \ln[2N_v C_n^0 / (2̃n/̃C_n + ̃p/̃C_p^0)] , \]
\[ ε_{in}^- = ε_c - kT \ln[2N_v C_n^- / (̃n/̃C_n + ̃p/̃C_p^-)] - U , \]

where Nv is the effective density of conduction band states above εc. The generation rate dependence of these quasi-Fermi levels is illustrated in Fig. 11, together with the DOS distribution assumed for calculation.

The first term w on the right hand side of Eq. (13) is usually neglected when compared with the last three terms that represent the effects of electron trapping at the conduction BT states and the DB states. Each term consists of the DOS distribution broadened by convoluting a hyperbolic secant function with a width of kT and a peak shifting with ω. The DB contribution is made of a mixture coming from different energy intervals, εin<ε<εc (third term) and εin−<ε<εin (fourth term). The possible mixing is generally a source of uncertainty in the analysis of experimental results by means of Eq. (13). In this regard, the inference that Cn ≫ Cn permits a useful and realistic approximation. The inequality suggests a larger contribution from the third term than from the fourth term, and hence simplifies Eq. (13) into

\[ \text{Im}[g̃(ω)/ñ(ω)] = C_n \int_{ε_{in}}^{ε_c} dε N^{BT}(ε) \text{sech}[(ε - ε_w)/kT]/2 \]
\[ + C_p^+ \int_{0}^{ε_{in}} dε N^{DB}(ε) \text{sech}[(ε - ε_w^+)/kT]/2. \] (14)

The validity of Eq. (14) has been confirmed by the model calculation with rcap=100. Namely, the approximation for \text{Im}[g̃(ω)/ñ(ω)] is justifiable, consistently with the replication of the spectral features shown by Re[μMPC].

Figure 12 displays the frequency dependence of Im[iαMPC] calculated from the experimental data for μc-Si:H and a-Si:H samples. Each curve corresponds to the result for the different generation rates shown in Fig. 8. The solid line represents a merger of the high frequency parts.
sample, the equilibrium electron density was calculated to be \( n_{eq}^f \approx 10^9 \text{ cm}^{-3} \), from the dark conductivity, yielding an estimated value of \( C_n^+ \approx 10^{-5} - 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) for the peak frequency \( \omega/2\pi \approx 100 \text{ Hz} \). On the other hand, for \( \mu_c\text{-Si:H} \), assuming the equilibrium-Fermi level to be lying at center of the band gap \( E_g \), corresponds to \( n_{eq}^f \approx 10^{10} \text{ cm}^{-3} \). Then, the peak observed at \( \omega/2\pi \approx 10 \text{ kHz} \) leads us to conclude that the \( C_n^+ \) value for \( \mu_c\text{-Si:H} \) is comparable to that for \( a\text{-Si:H} \). This confirms that DB defects in both materials have a very similar character.

VI. SUMMARY AND CONCLUSIONS

We have investigated photocarrier transport and the localized states in undoped \( \mu_c\text{-Si:H} \) by means of the MPC technique. The experiments show that the photocarrier drift mobility varies systematically with the crystalline grain size, the volume fraction, as well as the transport direction. The drift mobility measured in the coplanar electrode configuration increases with the volume fraction while a lower mobility is observed for smaller grains. The measurement in the sandwich arrangement reveals that the drift mobility in the direction perpendicular to the substrate is 1 order of magnitude higher than parallel to the substrate. The observations indicate that transport takes place via a grain-to-grain carrier delivery, and reflects the connectivity and the geometry of grains included in the material. These effects are discussed with two basic models. The effective-medium model brings into light the percolation process involved in the transport, and satisfactorily accounts for the drift mobility increase with the volume fraction observed in the experiment. The lower drift mobility for smaller grains proves that the grain boundary bottlenecks the percolation transport. The boundary-limited random walks model reasonably links the grain geometry to the transport anisotropy. Apart from the variation of drift mobility magnitude, the frequency spectra and generation rate dependence are also extensively discussed in comparison with those of \( a\text{-Si:H} \). The comparative study suggests that DB states contained in these materials have a very similar character. Based on the numerical simulation as well as on a direct evaluation from the measurements, we interpret the experimental results as indicating that common to both materials, the charged DB state possesses a higher capture efficiency than neutral ones.

ACKNOWLEDGMENT

The authors greatly acknowledge Dr. T. Matsui (National Institute of Advanced Industrial Science and Technology, Japan) for supplying \( \mu_c\text{-Si:H} \) samples which were prepared in his work at the Graduate School of Engineering Science, Osaka University.

APPENDIX: ANALYSIS OF SHOCKLEY-READ EQUATIONS

For the sake of simplicity, we consider a single species of monovalent states with an energy distribution \( N(\epsilon) \), through which electronic transitions occur at rates \( n^f(t)C_n \), \( p^f(t)C_p \), \( e_n(\epsilon) \), and \( e_p(\epsilon) \). According to the Shockley–Read formalism, the rate equation for electron occupation function \( f(\epsilon,t) \) is given by Eq. (11). The continuity equations for free carriers \( n^f(t) \) and \( p^f(t) \) are expressed as Eqs. (12a) and (12b), respectively, replacing \( N^{BT}(\epsilon) \) by \( N(\epsilon) \) and equating \( N^{DB}(\epsilon) \) to zero. It is easy to calculate the steady-state occupation function, which is written as

\[
\bar{f}(\epsilon) = \frac{[\bar{n}^fC_n + e_n(\epsilon)]/\rho(\epsilon)},
\]

with the sum of transition rates \( \rho(\epsilon) = \bar{n}^fC_n + \bar{p}^fC_p + e_n(\epsilon) + e_p(\epsilon) \). The modulated part of the occupation function involves two components relative to electrons and holes

\[
\bar{f}(\epsilon,\omega) = \bar{n}^f(\omega)\gamma_n(\epsilon,\omega) - \bar{p}^f(\omega)\gamma_p(\epsilon,\omega),
\]

where the coefficients \( \gamma_n,\gamma_p(\epsilon,\omega) \) are expressed as

\[
\gamma_n(\epsilon,\omega) = C_n[1 - \bar{f}(\epsilon)]/[i\omega + \rho(\epsilon)],
\]

\[
\gamma_p(\epsilon,\omega) = C_p\bar{f}(\epsilon)/[i\omega + \rho(\epsilon)].
\]

In terms of Eq. (A2), it is natural to express the trapped carrier densities as

\[
\bar{n}^f(\omega) = \bar{n}^f(\omega)\Gamma_n(\omega),
\]

\[
\bar{p}^f(\omega) = \bar{p}^f(\omega)\Gamma_p(\omega),
\]

with the energy integrals

\[
\Gamma_n(\omega) = \int d\epsilon N(\epsilon)\gamma_n(\epsilon,\omega).
\]

The total electron and hole densities must satisfy the charge neutrality, which is exactly shown by the following equality:

\[
\bar{n}(\omega) = \bar{n}^f(\omega) + \bar{p}^f(\omega) = \bar{n}^f(\omega) + \bar{p}^f(\omega).
\]

The drift mobility \( \mu(\omega) \) defined as \( \bar{v}(\omega) = q[\mu_n^f\bar{n}^f(\omega) + \mu_p^f\bar{p}^f(\omega)] \) is explicitly given by

\[
\mu(\omega) = \frac{\mu_n^f}{1 + \Gamma_n(\omega)} + \frac{\mu_p^f}{1 + \Gamma_p(\omega)}.
\]

Note that the electron-related term in Eq. (A6) coincides with the right hand side of Eq. (9). On the other hand, the average lifetime defined as \( \bar{\tau}(\omega)/\bar{g}(\omega) = 1/[i\omega + 1/\tau(\omega)] \) is found to be

\[
\frac{1}{\tau(\omega)} = \frac{1}{[1 + \Gamma_n(\omega)]\tau_n(\omega)} + \frac{1}{[1 + \Gamma_p(\omega)]\tau_p(\omega)},
\]

where

\[
1/\tau_n(\omega) = \int d\epsilon N(\epsilon)\gamma_n(\epsilon,\omega)[\bar{p}^fC_p + e_p(\epsilon)],
\]

\[
1/\tau_p(\omega) = \int d\epsilon N(\epsilon)\gamma_p(\epsilon,\omega)[\bar{n}^fC_n + e_n(\epsilon)].
\]